TECHNICAL CONSIDERATIONS FOR INVESTIGATING 1,2,3-TRICHLOROPROPANE SUBSURFACE CONTAMINATION IN SAN GABRIEL VALLEY AREA 3

August 2005

Acronyms and Abbreviations

°C degrees Celsius

 μ g/L microgram(s) per liter

μg/m³ microgram(s) per cubic meter

μg/kg microgram(s) per kilogram

1,2,3-TCP 1,2,3-trichloropropane

atm-m³/mol atmosphere-cubic meter per mole

ATSDR Agency for Toxic Substances and Disease Registry

bgs below ground surface

CAS Chemical Abstract System

CHRIS Chemical Hazard Response Information System

DHS California Department of Health Services

DLR detection limit for reporting

DNAPL dense nonaqueous-phase liquid

DTSC Department of Toxic Substances Control

ELAP Environmental Laboratory Accreditation Program

EPA United States Environmental Protection Agency

ETI EnviroMetal Technologies, Inc.

FID flame ionization detector g/cm³ gram per cubic centimeter

g/L gram per liter

GC/MS gas chromatography/mass spectrometry

gpm gallons per minute HCl hydrogen chloride $HiPOx^{TM}$ $HiperOxidation^{TM}$

HRC® Hydrogen Release Compound®

IRIS Integrated Risk Information System

ITRC Interstate Technology and Regulatory Council

LARWQCB Los Angeles Regional Water Quality Control Board

LGAC liquid-phase granular activated carbon

LLE liquid-liquid extraction m³/mol cubic meter per mole

MCAS Marine Corps Air Station

MCL maximum contaminant level

mg/kg milligram(s) per kilogram

ml millilter

mm Hg millimeter mercury

mol/kg-bar mole per kilogram-bar

mol/kg-atm mole per kilogram-atmosphere

MTBE methyl tertiary butyl ether

NAVFAC Naval Facilities Engineering Command

ND nondetect

NIOSH National Institute for Occupational Safety and Health

NL notification level

NTU nephelometric turbidity unit

OSHA Occupational Safety and Health Administration

OVA organic vapor analyzer

Pa-m³/mol Pascal-cubic meter per mole

PCE tetrachloroethene

ppbv part(s) per billion by volume

ppm part(s) per million

ppmv part(s) per million by volume

PRB Permeable Reactive Barrier

PRG preliminary remediation goal

PT purge and trap
QC quality control

RWQCB Regional Water Quality Control Board

SERDP Strategic Environmental Response and Development Program

SGV San Gabriel Valley

SIM selective ion monitoring

DEN/052280001.DOC III

SNARL Suggested No-Adverse Response Level

SOW statement of work

SRL DHS Sanitation and Radiation Laboratories

SS stainless steel

SVE soil vapor extraction

TCE trichloroethene

TCP-d5 1,2,3-Trichloropropane-deuterated fifth hydrogen atom

TDS total dissolved solids

TIC tentatively identified compound

TRI Toxic Release Inventory

U.S. United States

UCMR unregulated contaminant for which monitoring is required

UST underground storage tank

VOA volatile organic analysis

VOC volatile organic compound

WHO World Health Organization

Technical Considerations for Investigating 1,2,3-Trichloropropane Subsurface Contamination in San Gabriel Valley Area 3

1. Purpose and Scope

This document has been prepared to provide technical considerations for investigating 1,2,3-TCP subsurface contamination in San Gabriel Valley Area 3, which includes the City of San Gabriel, and parts of Alhambra, Rosemead, San Marino, South Pasadena, Temple City, and unincorporated Los Angeles County.

The body of this document provides information on investigation and sampling strategies, sampling methods, analytical methods, and remediation and treatment for 1,2,3-TCP. Information on chemical properties, environmental fate and transport, regulatory levels, and health risk information is provided in a series of appendices.

2. Investigation and Sampling Strategies

Because of the chemical properties of 1,2,3-TCP (volatility, solubility, and mobility; see Appendix A), a combination of environmental media will potentially need to be sampled to adequately investigate subsurface 1,2,3-TCP contamination; the combination of media will include soil, groundwater, and potentially soil gas (if an actual near-surface source area has been identified). Initiating potential source investigations using a soil gas survey may not be the most effective approach to identifying an area of a 1,2,3-TCP release, based on past experience at the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California. A summary of site investigation methods and descriptions is provided in Table 2-1.

TABLE 2-1
Summary of Investigation Methods and Descriptions

Investigation Method	Description
Review of Groundwater Monitoring Data	Prior to the development of DHS low-level analytical methods in 2002, the reporting limit for 1,2,3-TCP was typically as high as 10 μ g/L, well above the current DHS NL of 0.005 μ g/L. 1,2,3-TCP may also have been reported as a tentatively identified compound (TIC) in historic monitoring (i.e., analytical) data at concentrations exceeding approximately 90 μ g/L. Therefore, historical monitoring data should be reviewed to assess whether wells need to be resampled for 1,2,3-TCP using low-level analytical methods that permit comparison to the current NL.
Soil Gas Sampling	The success of soil gas surveys may be limited for investigating potential 1,2,3-TCP releases. Therefore, base soil gas surveys on an evaluation of prior facility operations focusing on areas where 1,2,3-TCP releases are likely to have occurred. The need for performing focused soil gas surveys, as opposed to comprehensive general and unfocused soil gas surveys, is based on prior experience at the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank).

TABLE 2-1
Summary of Investigation Methods and Descriptions

Investigation Method	Description
Subsurface Soil Sampling	Collect and analyze soil samples every 5 to 10 feet over the entire depth of a boring, because the detection of 1,2,3-TCP may be limited to small stratigraphic lenses over short intervals, as observed in San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank). Alternatively, select soil samples for analysis according to observed elevated head space readings, as measured with an organic vapor analyzer (OVA) or flame ionization detector (FID).
	The traditional approach for collecting and analyzing subsurface soil samples by direct-push methods, a California modified soil sampler, or equivalent is recommended.
Groundwater Sampling	Collect groundwater samples for 1,2,3-TCP analysis from existing monitoring and production wells, and install new monitoring wells at key locations to help further refine the interpreted extent of 1,2,3-TCP contamination in groundwater.

3. Sampling Methods

Recommendations for methods of collecting soil, groundwater, and soil gas samples for 1,2,3-TCP analyses are provided in this section. All sampling methods are listed and briefly described in Table 3-1. Sections 3.1, 3.2, and 3.3 provide additional details on each medium. Analytical methods are discussed in Section 4.

3.1 Groundwater

Groundwater samples may be collected from production wells, from conventional groundwater monitoring wells, from multilevel monitoring wells, and with diffusion bag samplers. In situ (depth-specific) groundwater samples may be collected to characterize the vertical extent of 1,2,3-TCP groundwater contamination.

Monitoring Wells

Sample collection from conventional and multilevel monitoring wells is the most common and direct method for detecting and monitoring 1,2,3-TCP in groundwater. A low-flow sampling method is recommended to minimize 1,2,3-TCP losses due to volatilization from turbulence within the well and during filling of sample containers. Samples collected in this manner will yield laboratory analytical results that are more representative of actual in situ groundwater concentrations.

Diffusion Bag Samplers

Vroblesh and Campbell (2001) reported that when using polyethylene-based passive diffusion samplers for volatile organic compounds (VOCs), concentrations of 1,2,3-TCP measured in samples collected with the diffusion bag sampler were within 10 percent of the concentrations in ambient water. This close agreement indicates that diffusion bag samplers are a viable alternative for collection of groundwater samples for analysis of 1,2,3-TCP. If a series of bags is suspended at different depths in a well, a vertical profile of 1,2,3-TCP concentrations may be obtained, assuming that the well is not acting as a conduit for vertical groundwater flow (which would result in nonrepresentative samples). This method is best suited for detailed profiling in wells with relatively short screen intervals (i.e., 50 feet or less). Procedures for use of diffusion bag samplers are provided in Interstate Technology and Regulatory Council guidance (ITRC, 2004).

TABLE 3-1 1,2,3-TCP Sampling Methods

Media	Sampling Method	Sample Container
Groundwater		
Groundwater – in situ samples	HydroPunch™ sampler (collect groundwater sample with small-diameter bailer inside HydroPunch™	40-milliliter (ml) VOA vial, hydrogen chloride (HCl) to pH <2, no headspace, cooled to 4 degrees Celsius (°C).
	assembly, decant to volatile organic analysis [VOA] vial).	Cool glass vial to 4°C immediately upon retrieval; submit to laboratory for analysis.
	BAT TM system groundwater sampler (evacuated 120-ml glass vial) is filled when septa is punctured in the subsurface.	Immediately transfer liquid sample to 40-ml VOA vial, HCl to pH <2, no headspace, cool to 4°C.
	SimulProbe [™] (able to collect simultaneous soil and groundwater samples).	NOTE: Given the depth to groundwater in San Gabriel Valley (SGV) Area 3 (275 to 300 feet below ground surface [bgs]), the cost to collect in situ groundwater samples below
	NOTE: Use of in situ, depth-specific samples permits characterization of the vertical extent of 1,2,3-TCP contamination.	the water table may be cost prohibitive. Depending on the depth of sample collection, these in situ methods may need to be used in combination with subsurface drilling methods.
Groundwater production wells	Fill sample container directly from wellhead tap, taking care to minimize sample aeration.	40-ml VOA vial, HCl to pH <2, no headspace, cool to $4^{\circ}\text{C}.$
Groundwater monitoring well	Dedicated pump (low-flow method preferred).	Directly fill 40-ml VOA vial, HCl to pH <2, no headspace, cool to 4°C.
	Diffusion bag sampler(s) (allow to equilibrate per instructions).	Carefully decant sample(s) into 40-ml VOA vial(s), HCl to pH <2, no headspace, cool to
	NOTE: With the aide of multiple sampler collection devices, a vertical concentration profile may be obtained.	4°C. NOTE: Vroblesh and Campbell (2001) report that when using polyethylene-based passive diffusion samplers for VOCs, the concentrations of 1,2,3-TCP measured with the diffusion bag sampler were within 10 percent of the concentration in ambient water.
Multilevel groundwater monitoring well	Use multilevel (e.g., Westbay® or other) sampling equipment to collect groundwater sample.	Fill 40-ml VOA vial directly from sample container, HCl to pH <2, no headspace, cool to 4°C.
Soil		
Soil – surface	Sample directly with Encore sampler.	Encore sampler, cooled to 4°C.
	Sample collection in a glass jar may be acceptable if soil conditions (e.g., the presence of gravel) prevents the use of an Encore sampler. This will require approval on a case-by-case basis. If approved, collect the grab sample with stainless steel spade, packing soil tightly into jar.	4-ounce glass jar (no headspace), cooled to 4°C.

TABLE 3-1 1,2,3-TCP Sampling Methods

Media	Sampling Method	Sample Container
Soil – subsurface	Direct push sampler	Brass or stainless steel (SS) sample sleeve;
	Piston sampler	seal end with Teflon tape, foil, and plastic end caps; cooled to 4°C.
	California modified soil sampler	
	SimulProbe™ (able to collect simultaneous soil and groundwater or soil and soil gas samples).	
Soil Gas		
Soil Gas	Install temporary or permanent soil gas sampling probe, purge, and sample per Los Angeles Regional Water Quality Control Board (LARWQCB)/Department of Toxic Substances Control (DTSC) guidance (2003).	Syringes, glass bulbs wrapped in Aluminum foil, SUMMA™ canisters.

In Situ Groundwater Sampling

In situ (depth-specific) sampling during drilling of monitoring wells can be performed using a HydroPunchTM, SimulProbeTM, or BATTM sampler in order to assess the vertical extent of 1,2,3-TCP groundwater contamination. However, given the depth to groundwater in the central portion of SGV Area 3 (275 to 300 feet bgs), the use of this approach as a screening technique likely would be cost prohibitive and time consuming.

3.2 Soil

Soil samples for analysis should be collected in Encore samplers to reduce 1,2,3-TCP losses from volatilization. Direct-push samples collected in stainless-steel or brass sleeves should be sealed with Teflon tape, foil, and plastic end caps. For samples of loose soil with gravel or coarse, loose sand or gravel that cannot be sampled with an Encore sampler, the soil should be packed tightly into a 4-ounce glass jar and the cap closed tightly. It should be noted that given the moderate volatility of 1,2,3-TCP, surface soil samples are unlikely to contain detectable concentrations of 1,2,3-TCP. Consequently, an alternative approach to characterizing concentrations of 1,2,3-TCP in soil would be to use heated soil head space field analyses, for example, during screening-level investigation of a site. All samples should be placed on ice immediately and maintained at 4°C prior to analysis.

Subsurface samples can be selected for submittal to a laboratory for 1,2,3-TCP analysis based on headspace concentrations, visible staining, or odor. Concentrations of 1,2,3-TCP are expected to be higher in fine-grained materials (e.g., silt), than in coarse-grained materials (e.g., gravel), where 1,2,3-TCP would volatize more easily in the vadose zone or dissolve more readily in the saturated zone (i.e., below the groundwater table).

3.3 Soil Gas

Little information is available on the effectiveness of soil gas surveys in assessing sources and releases of 1,2,3-TCP and the extent of 1,2,3-TCP soil contamination. A soil gas survey was completed during 2003 at a site in the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California. However, 1,2,3-TCP was not detected in any soil gas samples

above the detection limit of 1 μ g/L. For this reason, until additional soil gas investigations in the United States (U.S.) showing effective quantification of 1,2,3-TCP in soil gas at a range of concentrations have been documented, soil gas surveys are not anticipated to be particularly effective for investigating 1,2,3-TCP subsurface contamination. A combination of subsurface soil samples, groundwater sampling, and potentially soil gas sampling near suspected releases is expected to be the most effective approach to investigating 1,2,3-TCP subsurface contamination.

LARWQCB-lead investigations at facilities in the SGV where suspected releases of VOCs (e.g., tricholorethene [TCE] or tetrachlorethene [PCE]) have occurred typically begin with a soil gas survey, which has been shown to be a cost-effective strategy. However, because 1,2,3-TCP is less volatile than PCE or TCE (see Appendix A) and more difficult to detect, these limitations need to be considered when designing a soil gas survey to help locate potential 1,2,3-TCP releases. It is recommended that evaluation of operations at the facility or business be performed first, so that collection of soil gas samples can be focused in areas where an actual release may have occurred and, therefore, where elevated subsurface concentrations are expected. This approach may be more effective than using a sampling grid approach for screening a facility for potential 1,2,3-TCP releases.

4. Analytical Methods

A summary of recommended analytical methods for the analysis of 1,2,3-TCP in soil, soil gas, and groundwater, is provided in this section.

4.1 Groundwater

Because accepted methods (see Section 3) generally result in collection of samples with low levels of turbidity (e.g., less than 5 nephelometric turbidity units [NTUs]) from monitoring or production wells, most groundwater samples can be analyzed using methods developed for (unfiltered) drinking water. DHS has developed and approved two methods for analysis of water samples (including groundwater) for public (drinking) water systems that are capable of meeting the DHS detection limit for reporting (DLR) of 0.005 µg/L for 1,2,3-TCP (consistent with the NL of 0.005 µg/L): DHS purge and trap gas chromatography/mass spectrometry (PT-GC/MS) and DHS liquid-liquid extraction GC/MS (LLE-GC/MS). In addition, DHS has approved the use of U.S. Environmental Protection Agency (EPA) Methods 504.1 and 551.1 by laboratories that can achieve the DLR without implementing method modifications. These four DHS-approved methods are summarized in Table 4-1. It should be noted that when using EPA Methods 504.1 or 551.1 on samples with high total dissolved solids (TDS) or VOC content, or other interferents that preclude unambiguous identification, 1,2,3-TCP detection should be confirmed with one of the DHS GC/MS methods above. The DHS methods are recommended for definitive identification and quantification, especially for verifying the presence of 1,2,3-TCP at concentrations close to the NL. It should be noted that samples from essentially all of the active production wells in SGV Area 3, most of which are used to supply (unfiltered) drinking water, have been analyzed using one of the DHS methods (see Appendix B, unregulated contaminant for which monitoring is required [UCMR]).

TABLE 4-1
DHS-Approved Analytical Methods for 1,2,3-TCP in Water

Method	Detection Limit (μg/L)	Sample Container	Holding Time	Approximate Cost per Sample
DHS PT-GC/MS*	0.005	40-ml vial, HCl to pH <2; cooled to 4°C	14 days	\$150
DHS LLE-GC/MS	0.005	1-L amber bottle; cooled to 4°C	14 days before extraction; 24 hours for extract analysis	\$225
EPA 504.1	Varies by laboratory; typical detection limits in the past have been 0.02 µg/L	40-ml vial with sodium thiosulfate; cooled to 4°C	14 days before extraction; 24 hours for extract analysis	\$85
EPA 551.1	Varies by laboratory; one laboratory reported a 0.008 µg/L detection limit	60-ml vial with ammonium chloride; cooled to 4°C	14 days before extraction; 14 days for extract analysis	NA

^{*}Used by EPA Region 9 for groundwater monitoring samples in Area 3.

For all of these methods, the laboratory should be provided with a statement of work (SOW) that defines the needed quality control (QC) for the analyses to ensure that reproducible, comparable, and defensible data are generated. The QC specifications should include requirements for initial and continuing calibration, instrument tuning, internal standards, laboratory control standard, matrix spikes, duplicates, method detection limits, and documentation. The project-specific SOW should identify the specific QC procedures, level of effort (the frequency of the runs), acceptable QC limits, and corrective action requirements.

DHS Analytical Methods

The DHS Sanitation and Radiation Laboratories (SRL) have developed two GC/MS methods (PT-GC/MS and LLE-GC/MS) that are capable of 1,2,3-TCP quantification at the DLR. In February 2002, DHS published the two new analytical methods, listed below.

- Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry (DHS PT-GC/MS). http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyPT-GCMS.pdf.
- Determination of 1,2,3-Trichloropropane in Drinking Water by Continuous Liquid-Liquid Extraction and Gas Chromatography/Mass Spectrometry (DHS LLE-GC/MS). http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyLLE-GCMS.pdf.

Both methods use GC/MS in the selective ion monitoring (SIM) mode and isotope dilution to meet the low DLR. Quantitation is performed using isotope dilution with 1,2,3-Trichloropropane-deuterated fifth hydrogen atom (TCP-d5). The presence of VOCs that co-elute or overlap with TCP or TCP-d5, and that yield the same fragment ions as TCP or TCP-d5, can be a major source of error in both these methods. Due to the extreme sensitivity of these methods, even low abundances of these ions can result in severe interference when the interfering compound is present at sufficiently high concentrations. The following compounds have the potential to interfere: trans-1,4-dichloro-2-butene (m/z 75 ion), isopropylbenzene (m/z 75 ion), and o-xylene (m/z 79 ion). QC data for individual sample batches should be reviewed to evaluate the impact of these interferences on analytical data.

The list of laboratories certified by DHS under the Environmental Laboratory Accreditation Program (ELAP) to perform 1,2,3-TCP analysis in drinking water is available at http://www.dhs.ca.gov/ps/ls/elap/html/lablist.htm.

Other Analytical Methods

1,2,3-TCP is listed as an analyte in water for EPA Methods 502.2, 524.2, and 8260. These methods were used commonly in the past for the analysis of 1,2,3-TCP in water, and are currently used in some applications where 1,2,3-TCP is not the primary target analyte and where other chlorinated solvents are of primary concern (e.g., TCE, PCE, etc.). However, due to the fact that the 1,2,3-TCP detection limits are much higher than the NL for 1,2,3-TCP (0.005 μ g/L), EPA Methods 502.2, 524.2, and 8260 are not DHS-approved for analysis of 1,2,3-TCP in drinking water (Table 4-2). Nonetheless, EPA Methods 524.2 and 8260 using the SIM mode have been used successfully for the analysis of 1,2,3-TCP in water by some laboratories to achieve a detection limit of 0.002 μ g/L and 0.005 μ g/L, respectively. The price of the EPA Method 524.2 or 8260 analyses is approximately doubled when using the SIM mode (up to \$500 per sample).

It should be noted that for facility investigations to support an EPA site investigation or for a drinking water source, the DHS-approved analytical methods listed in Table 4-1 are recommended, not the alternative methods listed in Table 4-2.

TABLE 4-2 Other Analytical Methods for 1,2,3-TCP in Water

Method	Detection Limit	Sample Container	Holding Time	Approximate Cost per Sample
EPA 502.2	0.4 μg/L	40-ml vial with ascorbic acid*; HCl to pH <2; cooled to 4°C	14 days	\$110 to \$275
EPA 524.2 **	0.03 μg/L	40-ml vial with ascorbic acid*; HCl to pH <2; cooled to 4°C	14 days	\$225 to \$275
EPA 8260	0.005 μg/L	40-ml vial with ascorbic acid; HCl to pH <2; cooled to 4°C	14 days	\$500

Use of ascorbic acid is recommended in samples collected from some public drinking water systems to remove any chlorine that may be in the water. Ascorbic acid is a very weak acid that is not be suitable for lowering the pH of the sample (HCl is instead used for that purpose).

4.2 Soil

Recommended methods for the analysis of 1,2,3-TCP in soil are provided in Table 4-3. California has not proposed reporting limits for 1,2,3-TCP in soils; however, EPA preliminary remediation goals (PRGs) for soils are commonly used to establish upper boundaries of acceptable target reporting limits. The EPA Region 9 PRGs for 1,2,3-TCP are 0.034 milligram per kilogram (mg/kg) for soil in residential areas (10⁻⁶ cancer risk) and 0.076 mg/kg for soil in industrial areas (10⁻⁶ cancer risk) (see Appendix B). As shown in Table 4-3, analyses using EPA Methods 8021B and 8260B can meet these target reporting limits. The detection limit cited for 1,2,3-TCP using EPA Method 8270C (Table 4-3) is an estimate based on analysis of similar compounds. To quantify 1,2,3-TCP at concentrations lower than the EPA PRGs, the use of Method 8270C with SIM would be necessary.

EPA 524.2 has recently been used in the SIM mode for the analysis of 1,2,3-TCP with a the detection limit of $0.002 \mu g/L$.

TABLE 4-3
Analytical Methods for 1,2,3-TCP in Soil

Method	Detection Limit (μg/kg)	Sample Container	Holding Time	Approximate Cost per Sample
EPA 8021B	Approximately 10 micrograms per kilogram (µg/kg)	Encore sampler, brass or stainless- steel sleeve, cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours. Sample should not be frozen below -20°C due to potential problems with seals and the loss of constituents upon sample thawing.	\$150
EPA 8260B	Approximately 5 μg/kg	Encore sampler, brass or stainless- steel sleeve, cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours. Sample should not be frozen below -20°C due to potential problems with seals and the loss of constituents upon sample thawing.	\$225 to \$350
EPA 8270C	Approximately 330 to 660 μg/kg	Encore sampler, brass or stainless- steel sleeve, cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours. Sample should not be frozen below -20°C due to potential problems with seals and the loss of constituents upon sample thawing.	\$195

To minimize analyte loss, EPA recommends collecting a soil sample in an Encore sampler, or extruding the sample into an empty sealed vial, cooling to 4 ± 2 °C for no more than 48 hours, then freezing to -7°C upon laboratory receipt.

No specific interferences have been identified for the methods presented in Table 4-3; however, matrix-specific interferences potentially may be present.

4.3 Soil Gas

Soil gas surveys have been used to investigate suspected 1,2,3-TCP sources in groundwater basins like the SGV to a very limited extent. A soil gas investigation was performed at a facility in the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California. Soil vapor samples were analyzed using an unpublished procedure that involved a GC with an MS detector (GC/MS) in both "open scan" and SIM modes. Soil gas samples were collected either as whole samples in SUMMATM canisters or Tedlar® bags, or on charcoal/tenax tubes. Soil gas samples were analyzed either directly or using a tenax trap to collect 1,2,3-TCP prior to desorption into the GC/MS. The sensitivity of this unpublished GC/MS SIM method was approximately 0.1 to 0.2 part per billion by volume (ppbv).

Subsurface collection probes for the soil gas samples were placed at depths 20 to 30 feet above the groundwater table near a monitoring well in which 1,2,3-TCP had been previously detected at concentrations up to 200 μ g/L. Soil gas samples collected from these probes contained either very low, or nondetectable, concentrations of 1,2,3-TCP. The contractor performing the analysis noted that the analytical method was reliable, but suggested that the soil gas survey did not appear to be a reliable method for locating sources of 1,2,3-TCP contamination, because groundwater and soil analytical results did not correlate well to the soil gas analytical results. Ultimately, the contractor concluded that until further soil gas analysis research was performed, soil gas analysis for 1,2,3-TCP should be combined with 1,2,3-TCP analysis of soil and groundwater samples from the facility to confirm the presence, or the absence, of 1,2,3-TCP.

By using SIM, the 8260 detection limits can be reduced by orders of magnitude.

Methods for soil gas analysis should be selected based on the sampling method chosen (i.e., passive or active) and the intended use of the data. Field analysis using portable instrumentation, such as GC or GC/MS, may be performed, usually by a mobile laboratory, or samples may be shipped to an offsite laboratory. Offsite laboratory analysis generally is more expensive, but also more reliable, because more rigorous QC procedures are in place.

Currently, information and data regarding the sampling and analysis of 1,2,3-TCP in soil vapor/ ambient air are limited. National Institute for Occupational Safety and Health (NIOSH) Method 1003 is currently used for monitoring worker exposure in ambient air. The NIOSH method for offsite laboratory analysis involves extraction of the sample on a solid sorbent with carbon disulfide, and analysis by GC with an FID. The method requires the use of a charcoal tube for sample collection and analysis by a GC/FID, with a reporting limit of roughly 1 part per million by volume (ppmv). This NIOSH method lacks the sensitivity and selectivity required for most facility source investigations. Table 4-4 summarizes the methods that are available for 1,2,3-TCP analysis of soil gas. Method modifications to meet the project- or site-specific detection limits may need to be evaluated and considered.

TABLE 4-4
Analytical Methods for 1,2,3-TCP in Soil Gas

Method	Detection Limit	Sample Container	Holding Time	Approximate Cost per Sample
EPA 8260B	1 μg/L – vapor	Amber gas-tight glass bulb or SUMMA™ canister	4 hours for amber gas-tight glass bulb; 72 hours for SUMMA™ canister a	NA
NIOSH 1003	0.01 mg/ sample	Solid sorbent	None published, but analysis should be done as soon as possible to minimize analyte loss	NA
EPA TO-15	0.050 micrograms per cubic meter (μg/m³)	SUMMA™ canister	30 days	\$125

*LARWQCB requirement. NA – Not available.

5. Remediation and Treatment

5.1 Remediation

Only limited information is available on remediation of 1,2,3-TCP contamination. Potential remediation approaches are summarized in Table 5-1.

It should be noted that the effectiveness of the remediation approaches presented in Table 5-1 at low 1,2,3-TCP concentrations, such as those observed in SGV Area 3 (about 0.400 μ g/L or less), needs to be further assessed.

TABLE 5-1 Remediation Approaches for 1,2,3-TCP Contamination

Approach	Media	Description
Pump and Treat	Groundwater	Effective for containment or source control. Not expected to be cost effective for source remediation. See Table 5-2 for groundwater treatment approaches.
In Situ Vacuum Extraction and In Situ Oxidation.	Soil, Soil Gas (vapor), and Groundwater	Full-scale remediation of soils, bedrock, and groundwater is underway at the Tyson Superfund Site near Philadelphia, Pennsylvania, using in situ vacuum extraction of silty clay soils, dual extraction of water and vapor from underlying fractured sandstone, and collection and treatment of seep water. Vapor treatment uses activated carbon adsorption (Pezullo et al., 2005). Oxidants have been injected into the subsurface in areas of dense nonaqueous-phase liquid (DNAPL) containing 1,2,3-TCP to oxidize contaminants in the subsurface. The more volatile byproducts from the oxidation reactions are captured by the vacuum extraction system that is designed to recover these byproducts. It should be noted that because the Henry's Law constant for 1,2,3-TCP (3 x 10 ⁻⁴ atmosphere-cubic meter per mole (atm-m³/mol); see Appendix A) is below the 10 ⁻³ threshold commonly used to assess application of soil vapor extraction (SVE) as a stand-alone remedial alternative, vacuum extraction may not be the most effective remedial approach. This technique is applicable to soil gas concentrations from tens to thousands of μg/.m³ and total soil VOC concentrations of up to hundreds of thousands of mg/kg (i.e., percentage levels).
Dechlorination by Hydrogen Releasing Compounds	Groundwater	Use of Hydrogen Release Compound (HRC®) for in situ treatment of 1,2,3-TCP resulted in 99.9% reduction over 1,000 days at an unnamed site in California. HRC® has also been used at the John Taylor Fertilizers Company in Yuba City, CA (Regional Water Quality Control Board [RWQCB], 2004) and Western Farm Service, Inc. (RWQCB, 2002). HRC® is a product designed for in situ treatment of chlorinated solvents or any anaerobically degradable substance. HRC® slowly hydrolyzes releasing lactic acid, which is utilized by microbes to produce hydrogen, thereby inducing reductive dechlorination. This technique is applicable to concentrations ranging from less than 1 μg/L to 1 mg/L.
Permeable Reactive Barrier (PRB)	Groundwater	Zero-valent iron has been shown to reduce 1,2,3-TCP. Therefore, the application of PRB technology may be a viable for remediation of a shallow 1,2,3-TCP plume (Focht and Gillham, 1995; Vidic and Pohland, 1996). Others have described the feasibility of using a PRB for remediation of 1,2,3-TCP in groundwater (EPA, 1998).
		EnviroMetal Technologies, Inc. (ETI) has performed bench column testing to treat 1,2,3-TCP in groundwater. Treatability testing involved water from a site in California and use of a 100 percent commercially available granular iron supply. The influent concentration of 437 $\mu g/L$ 1,2,3-TCP declined to nondetectable concentrations during a 12-hour residence time at room temperature (ETI, 2005). Based on this testing, ETI is recommending the application of a granular iron PRB to treat 1,2,3-TCP groundwater contamination.
		Given the depth to groundwater in SGV Area 3 (275 to 300 feet bgs), a PRB could not be installed via a trench, but would likely need to be installed by injecting the materials into the subsurface via closely spaced wells.
In Situ Biodegradation	Groundwater	1,2,3-TCP is not readily biodegradable under aerobic conditions

TABLE 5-1
Remediation Approaches for 1,2,3-TCP Contamination

Approach	Media	Description
		and is only slowly transformed by bacteria under aerobic and anaerobic conditions (World Health Organization [WHO], 2003). Bosma (2002) has genetically engineered a strain of bacteria that can utilize 1,2,3-TCP as a food source. However, the microbial activity is insufficient to sustain bacterial growth. Peijnenburg, et al. (1998) observed the reductive dehalogenation of 1,2,3-TCP in anaerobic sediments. See Appendix A for additional discussion of 1,2,3-TCP biodegradation.
U.S. Department of Defense Strategic Environmental Response and Development Program (SERDP) Initiatives	Groundwater	The SERDP sponsors initiatives for innovative remediation approaches. The SERDP currently (April 2005) has a project (CU-1457) listed on their website (http://www.serdp.org/research/Cleanup.html) that involves investigating prospects for remediation of 1,2,3-TCP by natural and engineered abiotic degradation reactions.

5.2 Treatment

Although treatment of 1,2,3-TCP in groundwater is underway at some contaminated sites in the U.S., only limited information regarding the technologies is available at this time. The initial screening of groundwater treatment technologies presented in Table 5-2 was prepared based on experience at the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California.

TABLE 5-2
Ex Situ Groundwater Treatment Technology Screening for Removal of 1,2,3-TCP

Treatment Technology	Application Performance Opinion
Air Stripping	Poor
Liquid-Phase Granular Activated Carbon (LGAC) Adsorption	Very Good
Advanced Oxidation	Poor
Biological Reduction	Poor
Ion Exchange	NA
Reverse Osmosis	Fair
Zero-Valent Iron Dechlorination	Fair

NA - Not applicable

Key Treatment Technology Discussion

Ex situ treatment using LGAC adsorption is in use for treatment of 1,2,3-TCP in groundwater at the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California.

Typical LGAC vessel design flux (5 to 8 gallons per minute [gpm]/square foot) and empty bed contact time (10 minutes) assumptions have been used in developing an isotherm for 1,2,3-TCP using small-scale column test data and site data from the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California. Treatment of 1,2,3-TCP using LGAC appears to have an unusually long mass transfer zone, which is defined as the bed (i.e., carbon inside the vessel) depth required to reduce a specific VOC from inlet concentrations to a target concentration. For most VOCs (e.g., TCE and PCE), the mass transfer zone needed to remove 99 percent of the inlet VOC mass may

be about 1 to 2 feet of carbon bed depth. However, for 1,2,3-TCP, it appears that the mass transfer zone may be much longer; for example, up to 5 feet of carbon bed depth. This, in turn, results in earlier breakthrough (and higher carbon use) compared to most other common VOCs.

Advanced Oxidation

The HiperOxidationTM (HiPOxTM) process has been in use for treatment of methyl tertiary butyl ether (MTBE), commingled with comparatively minor concentrations of 1,2,3-TCP, at the former Marine Corps Air Station (MCAS) Tustin Underground Storage Tank (UST) Site 222 (Naval Facilities Engineering Command [NAVFAC], 2003). As of 2003, nearly 2,910 pounds of MTBE and 1 pound of 1,2,3-TCP had been removed from groundwater at the former MCAS Tustin site. Based on experience at former MCAS Tustin, the cost of operating the HiPOxTM treatment system is nearly three times the cost of operating an LGAC system for treatment of the 1,2,3-TCP groundwater contamination. Additional details on the operation of the HiPOxTM system to treat /remove 1,2,3-TCP and other chlorinated solvents in groundwater is provided by Dombeck (2005).

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Appendixes

- A Chemical Properties/Environmental Fate and Transport
- B Regulatory Levels
- C Health Risk Information



Appendix A Chemical Properties/Environmental Fate and Transport

Chemical Properties

1,2,3-Trichloropropane (1,2,3-TCP), which can be referred to using a variety of chemical names and identifiers (Table A-1), is a non-polar chlorinated alkane that is soluble in alcohol, ether, and chloroform and is slightly soluble in water. It dissolves oils, waxes, fats, chlorinated rubber, and numerous resins. It is sensitive to prolonged exposure to light and heat. It is reactive with chemically active metals, strong caustics, and oxidizers. When heated to decomposition, it yields highly toxic fumes of carbon monoxide, carbon dioxide, hydrogen chloride, phosgene, and other chlorinated compounds. Table A-2 lists chemical properties of 1,2,3-TCP and specifies how these properties relate to the behavior of 1,2,3-TCP in the environment.

Formula: C₃H₅Cl₃

Chemical Structure:

TABLE A-1 Chemical Name	s and Identifiers
Item	Description
Synonyms	allyl trichloride
	glycerin trichlorohydrin
	glycerol trichlorohydrin
	glyceryl trichlorohydrin
	trichlorohydrin
	trichloropropane
	1,2,3-TCP
	TCP
Identifiers	United Nations No.: 2810
	Chemical Abstract System (CAS) Registry No.: 96-18-4
	Chemical Hazard Response Information System (CHRIS): TCN
	Storet No.: 7743

TABLE A-2 Chemical Properties of 1.2.3-TCP

Property	Value	Reference	Environmental Efficacy	
Molecular Weight	147.44 g	Verschueren, 1996		
Density at 20°C (Water = 1)	1.42 gram per cubic centimeter (g/cm³)	Verschueren, 1996	More dense than groundwater, can act as DNAPL.	
Boiling Point	156 °C	WHO, 2003	Liquid at room temperature.	
Melting Point	-14.7 °C	WHO, 2003		
Vapor Pressure at 25°C	3.1 millimeter mercury (mm Hg)	ATSDR, 1992	Evaporates quickly at ambient temperatures; can be removed from surface water by evaporation.	
Air Saturation at 20°C	16 g/m ³	Verschueren, 1996		
Relative Vapor Density (Air=1)	5.1	WHO, 2003	Vapor is denser than air, can accumulate above the water table.	
Henry's Law Constant at 25°C	2.8 to 4.4 mole per kilogram-bar (mol/kg-bar)	NIST database	Volatile, but does not volatilize as readily as PCE, TCE; moderate volatilization from	
	22.83 Pascal-cubic meter per mole (Pa- m³/mol)	WHO, 2003	either dry or moist soil to the atmosphere.	
	3.17 x 10 ⁻⁴ atm-m ³ /mol	ATSDR, 1992		
Solubility at 25°C	1.75 g/L	WHO, 2003	Relatively insoluble, but up to 1,750 mg/L (1,750,000 µg/L) may be present in water.	
Octanol/Water Partition	2.54 (calculated)	WHO, 2003	The low K _{ow} value indicates	
Coefficient (log K _{ow})	2.27 (measured)	WHO, 2003	that 1,2,3-TCP is mobile in the environment.	
	1.98	ATSDR, 1992		
Organic Carbon Partition	68	NYSDEC (2005)	Expected to display high	
Coefficient (log K _{oc})	98 (calc. from solubility)	Lyman et al. (1982)	mobility in soil, and therefore has the potential to leach into groundwater primarily as 1,2,3-TCP.	

Table A-3 lists selected properties of 1,2,3-TCP relative to the properties of tetrachloroethene (PCE), trichloroethene (TCE), and 1,4-dioxane. Because PCE and TCE are the most prevalent volatile organic compounds (VOCs) in groundwater in San Gabriel Valley (SGV) Area 3, comparing the properties of 1,2,3-TCP to the properties of these VOCs can be useful in predicting the fate and transport of, and possible treatment options for, 1,2,3-TCP in SGV Area 3.

TABLE A-3 Chemical Properties of 1,2,3-TCP, PCE, TCE, and 1,4-Dioxane

Property	1,2,3- Trichloropropane	Tetrachloroethene	Trichloroethene	1,4-Dioxane	Reference
Molecular Weight	147.43	165.83	131.39	88.11	NIST database
Melting Point (°C)	-14	-22	-73	12	www.inchem.org
Boiling Point (°C)	156	121	87	101	www.inchem.org
Specific Gravity at approximately 20°C (Water = 1)	1.42	1.63	1.46	1.03	Verschueren, 1983
Vapor Pressure (kilopascals at 20°C)	0.29	1.9	7.8	4.1	www.inchem.org
Saturated Concentration (mg/L) in water at 20°C	1,750 ^a	126 ^b	415 ^b	miscible ^b	^a At 25 ^o C per WHO, 2003; ^b Verschueren, 1983
Relative Vapor Density at 20°C (Air=1)	5.1	5.8	4.5	3.0	www.inchem.org
Henry's Law Constant (atm-m³/mol) indicating volatility at 25°C	0.000344 ^c	0.0171 ^d	0.0102 ^d	0.00000488 ^c	^c Howard, 1993; ^d AWWA, 1999
Octanol/Water Partition Coefficient (log K _{ow})	2.3	2.9	2.4	-0.42	www.inchem.org
Organic Carbon Partition Coefficient (K_{oc})	68	277	126		NYSDEC, 2005
Biodegradation Half-Life in Soil (months) ^e	6 to 12	6 to 12	6 to 12	1 to 6	Howard, et al., 1991
Biodegradation Half-Life in Groundwater (months) ^e	12 to 24	12 to 24	11 to 53	4 to 24	Howard, et al., 1991
Notes:	mol/kg-atm - moles per kilogram-atmosphere at 25 degrees Celsius				

atm-m³/mol – atmosphere-cubic meter per mole at 25 degrees Celsius

^eScientific judgment based upon estimated aqueous aerobic biodegradation half-life.

°C - degrees Celsius

mg/L - milligrams per liter

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Based on the organic carbon partition coefficients (K_{oc}) shown in Table A-3, 1,2,3-TCP is more mobile in groundwater than PCE and TCE. The higher the K_{oc} value, the greater extent to which the chemical is adsorbed to organic material in the subsurface. Because 1,2,3-TCP has a lower K_{oc} value, it will adsorb to subsurface materials less readily than PCE or TCE and will travel at a rate closer to the average groundwater velocity compared to PCE and TCE. In this manner, 1,2,3-TCP released in groundwater should migrate further downgradient of a source compared to PCE and TCE. In addition, 1,2,3-TCP is more soluble than PCE and TCE; therefore, higher initial concentrations in groundwater are possible. Lower vapor pressure and Henry's Law Constant values indicate that 1,2,3-TCP is comparatively more difficult to detect in soil gas than PCE and TCE and would be much more difficult to treat by air stripping. If present in vadose zone soil, 1,2,3-TCP can be expected to preferentially reside in pore moisture based on its chemical properties. Once in the environment, 1,2,3-TCP is likely to display a resistance to aerobic biodegradation similar to PCE and/or TCE.

Environmental Fate and Transport

Abiotic Transformations

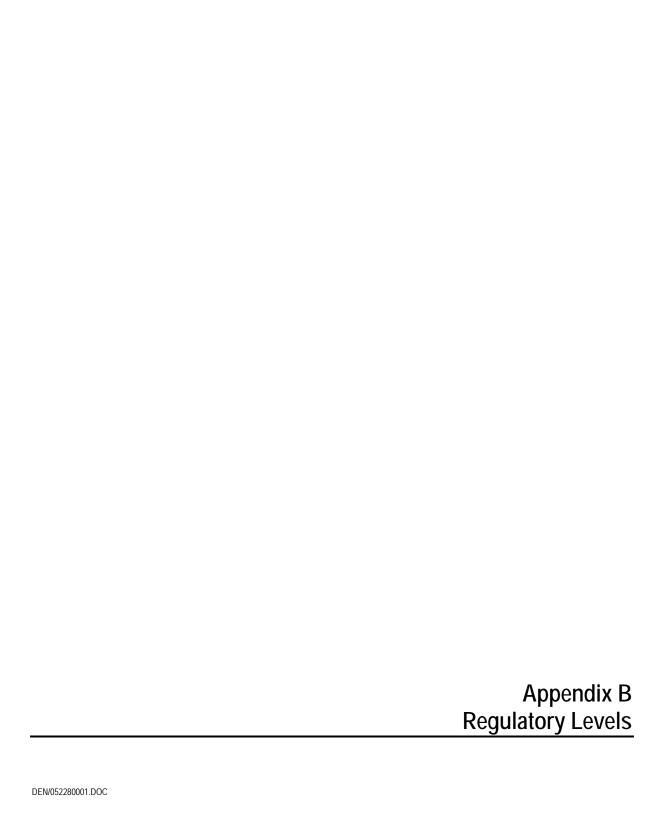
A calculated half life of 27.2 to 30.5 days for 1,2,3-TCP in the atmosphere has been reported. Therefore, 1,2,3-TCP released in the atmosphere might undergo very slow degradation in the presence of a sufficient concentration of photochemically produced hydroxyl radicals. Hydrolysis of 1,2,3-TCP in air appears to be of minor importance, with calculated half lives of 44 and 74 years (WHO, 2003).

Biotransformation and Degradation

1,2,3-TCP does not readily biodegrade in tests conducted under aerobic conditions. In a preliminary study, the co-oxidative transformation of 1,2,3-TCP by the ammonia oxidizing bacterium Nitrosomonas europaea was shown (Vanelli et al., 1990). More recent studies employing the methanotroph Methylosinus trichosporium demonstrated that 1,2,3-TCP is co-metabolized to a range of different chemicals, such as chlorinated propanols (Bosma and Janssen, 1998). However, attempts to isolate bacterial cultures that utilize 1,2,3-TCP as a sole source of carbon and energy have failed (WHO, 2003). Peijnenburg et al. (1998) observed the reductive transformation of 1,2,3-TCP in anaerobic sediments, and determined that reductive dehalogenation was the sole reaction taking place. Anderson et al. (1991) reported a lack of biodegradation of 1,2,3-TCP in clay loam.

For soil fumigants containing 1,3-dichloropropene and chloropropanes, biodegradation appears to be much more significant for 1,3-dichloropropene than either 1,2-dichloropropane or 1,2,3-TCP. 1,3-Dichloropropene in the vapor-phase will react with air as well as volatilize, biodegrade, and hydrolyze in soils and surface waters. Once 1,2-dichloropropane and 1,2,3-TCP have entered the groundwater, further breakdown products are unlikely to be generated, because both compounds are resistant to hydrolysis and biodegradation.

1,2,3-TCP is not readily biodegraded and is only slowly transformed by bacteria under aerobic and anaerobic conditions. In addition, 1,2,3-TCP has not been shown to bioaccumulate.



Appendix B Regulatory Levels

A summary of regulatory levels for 1,2,3-trichloropropane (1,2,3-TCP) is provided in Table B-1, followed by more detailed text descriptions.

TABLE B-1
Regulatory and Water Quality Levels

Regulatory Level	Agency	Concentration
Federal maximum contaminant level (MCL)	EPA, Region 9	NA
California MCL	DHS	NA
California Notification Level (NL)	DHS	0.005 µg/L
Detection Limit for Reporting (DLR)	DHS	0.005 μg/L
Preliminary Remediation Goals (PRGs)		
PRG – tap water (10 ⁻⁶ cancer risk)	EPA, Region 9	0.0056 μg/L
PRG – tap water (noncancer risk)		30 μg/L
PRG – residential soil (10 ⁻⁶ cancer risk)		0.034 mg/kg
PRG – residential soil (noncancer risk)		71 mg/kg
PRG – industrial soil (10 ⁻⁶ cancer risk)		0.076 mg/kg
PRG – industrial soil (noncancer risk)		270 mg/kg
EPA Integrated Risk Information System (IRIS) Reference Dose as a Drinking Water Level	EPA	42 μg/L
Drinking Water Health Advisory or Suggested No-Adverse Response Level (SNARL) for toxicity other than cancer risk	EPA	40 μg/L

Notes:

NA - not applicable (standard does not exist)

California Notification Level

In May 1999, the California Department of Health Services (DHS) Division of Drinking Water and Office of Health Hazard Assessment announced an action level (now referred to as a notification level [NL]) of 0.005 micrograms per liter (μ g/L) for 1,2,3-TCP. The NL is based on the categorization of 1,2,3-TCP as a probable human carcinogen, on the discovery of 1,2,3-TCP in groundwater at the San Fernando Valley Superfund Site (Area 1 – North Hollywood and Burbank), California, and over a concern that the chemical might find its way into public drinking water supplies.

Unregulated Contaminant for which Monitoring is Required Monitoring

In 2001, to obtain information about the presence of 1,2,3-TCP in drinking water sources, DHS adopted a regulation that included 1,2,3-TCP as an unregulated contaminant for which monitoring is

required (UCMR). For this monitoring, DHS developed protocols for analytical methods for 1,2,3-TCP at levels comparable to the NL of 0.005 μ g/L. Monitoring under the UCMR regulation was to have been completed by the end of 2003.

These regulations were adopted before the availability of analytical methods capable of achieving the DLR value of $0.005~\mu g/L$ for 1,2,3-TCP. Some utilities proceeded with monitoring, using insufficiently sensitive laboratory analyses with higher DLRs. Unfortunately, nondetects (NDs) reported using a method with a DLR higher than $0.005~\mu g/L$ provide DHS with inadequate information for setting standards. The DHS Sanitation and Radiation Laboratory developed an adequate analytical method and some commercial laboratories are able to achieve the $0.005-\mu g/L$ DLR with either EPA Method 504.1 or 551.1. Therefore, any utility reporting NDs for 1,2,3-TCP using a method with reporting levels of $0.010~\mu g/L$ or higher should perform confirmation testing using a method with a $0.005-\mu g/L$ DLR.

Notification of Exceedance of NL

A new law, effective January 1, 2005, requires that public water systems notify local governing bodies (e.g., city councils and county boards of supervisors) when NLs or MCLs for contaminants in drinking water supplies are exceeded. Even if notification occurred prior to that date under previous and different requirements, water system managers are encouraged to familiarize themselves with the new notification requirements and ensure that they are meeting these requirements.

EPA Region 9 PRGs

EPA Region 9 publishes PRGs for guidance in performing site remediation, feasibility studies, and risk assessments. PRGs for 1,2,3-TCP are provided with cancer and noncancer assumptions in Table B-1 (EPA Region 9, October 2004).



Appendix C Health Risk Information

Human exposure to 1,2,3-trichloropropane (1,2,3-TCP) can occur from inhalation, ingestion of contaminated water, dermal contact with contaminated soil or water, and working in a facility where 1,2,3-TCP is used. 1,2,3-TCP can be measured in blood, urine, and breath. However, it breaks down quickly and leaves the body in breath, urine, and feces.

1,2,3-TCP causes cancer in laboratory animals (EPA, 1997), which is the basis for the California Department of Health Services (DHS) notification level (NL). It is reasonably anticipated to be a human carcinogen (NTP, 2005). In 1999, 1,2,3-TCP was added to the list of chemicals known to the State of California to cause cancer [Title 22, California Code of Regulations, Section 12000].

Health Effects

The main adverse health effect from exposure to 1,2,3-TCP in both animals and people is damage to the respiratory system. Exposure to high levels (100 parts per million [ppm]) of 1,2,3-TCP for a short time can cause central nervous system damage, liver damage, and eye, skin, and throat irritation. Rats and mice died after breathing air containing 1,2,3-TCP. After swallowing 1,2,3-TCP at high levels, rats died from liver and kidney damage. At moderate nonlethal doses, rats had minor liver and kidney damage, blood disorders, and stomach irritation. Animals that swallowed low doses for most of their lives developed tumors in several organs. When applied to the skin of rabbits, 1,2,3-TCP caused severe irritation, followed by injury to internal organs.

In the Eighth Report on Carcinogens (1998), 1,2,3-TCP is listed, for the first time, as a substance reasonably anticipated to be a human carcinogen. It is also listed in the Toxic Release Inventory (TRI) as an Occupational Safety and Health Administration (OSHA) carcinogen. However, the Department of Health and Human Services, EPA, and the International Agency for Research on Cancer have not classified 1,2,3-TCP for carcinogenicity.